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# Czochralski growth of $Yb^{3+}$ and $Pr^{3+}$ doped Ca-fluoroapatite

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Pure, $Pr^{3+}$, and $Yb^{3+}$ doped Ca-fluoroapatite (Ca-FAP) crystals were grown by the Czochralski method. The effective distribution coefficient $k_{eff}$ for $Yb^{3+}$ was 0.5. For $Pr^{3+}$ a very high $k_{eff}$ of 1.4 was obtained. Values for $k_{eff}$ are discussed in terms of an elastic model accounting for the strain energy originating from the difference in the size of $Ln^{3+}$ ions. The $Ln^{3+}$ concentrations were measured by absorbance spectroscopy, by inductively coupled plasma optical emission spectroscopy, and by electron microprobe analyses.

The apatite structural family $[A_{10}(MO_4)_6X_2]$, represented by a large class of natural and synthetic compounds, crystallizes in a few different, but related, hexagonal and pseudohexagonal structures.[1,2] $Ca_5(PO_4)_3F$ (Ca-FAP), apatite, belongs to the hexagonal space group $P6_3/m$ with $Z = 2$.[3] The ten $Ca^{2+}$ ions are distributed over two crystallographically different sites: 4 $Ca^{2+}$ are at site I with site symmetry 3 and 9-fold coordination by $O^{2-}$; 6 $Ca^{2+}$ are at site II with 6-fold $O^{2-}$ and one $F^-$ coordination.[4] Lanthanide dopants predominantly enter the Ca(II) site which provides a low energy charge compensation mechanism[5]: The $Ln^{3+}$ ion substitutes for $Ca^{2+}$(II), whose nearest neighbor $F^-$ ion is replaced by an $O^{2-}$.[6] Because only one $F^-$ ion is available for bonding to every three Ca(II) ions, at most only two $Ln^{3+}$ ions for every ten $Ca^{2+}$ in the unit cell can enter the structure without creating an additional charge compensation mechanism.[5] In this study we found that co-doping with, e.g., $Na^+$ had no influence on the effective distribution coefficient $k_{eff}$ of $Yb^{3+}$.

$Yb^{3+}$ doped Ca-FAP and Sr-FAP are currently of interest because of efficient solid state laser properties when pumped by InGaAs diode sources.[7–9] Recently, a diode-pumped, Q-switched Sr–FAP : $Yb^{3+}$ laser (1047 nm) has been demonstrated.[9]

In this work we have explored Ca-FAP crystal growth for two reasons: (i) determination of the effective distribution coefficients $k_{eff}$ of $Yb^{3+}$ and $Pr^{3+}$, and (ii) the potential of the Ca-FAP host-lattice as a new material for $Pr^{3+}$ hyperfine pumped optical hole burning (H-OHB). An important parameter for the application of OHB in optical memories is the homogeneous linewidth of the holes, which is influenced by flip-flop processes of the nuclear magnetic moments of the host material.[10] In a previous study we have discussed possible low nuclear spin density host materials for $Pr^{3+}$ of $Eu^{3+}$ H-OHB.[10] However, a major drawback of selected compounds is that they showed only low doping levels and some effects of disorder in the nearest neighborhood of $Ln^{3+}$ due to a heterovalent mechanism of substitution. Although Ca-FAP will provide nuclear spins at P and F sites, it nevertheless bears the possibility of a particular mechanism for the charge compensation of $Ln^{3+}$. The mechanism discussed above implies that a $Pr^{3+}$ ion in the Ca-FAP lattice would be surrounded by 7 $O^{2-}$ ions whose only isotope with nonvanishing spin ($O^{17}$, $I = 5/2$, $\mu^{(N)} = -1.9\ \mu_N$) has a very low natural abundance (0.04%).[11] In the first coordination sphere of the $Pr^{3+}$ ion no nuclear magnetic moments could hence provide an efficient mechanism of broadening the homogeneous line.

In the following we describe the Czochralski growth of Ca-FAP doped either by $Yb^{3+}$ or $Pr^{3+}$ and the determination of the effective distribution coefficients $k_{eff}$. Obtained values are discussed in terms of an elastic model accounting for the strain energy originating from the difference in the size of $Ln^{3+}$ ions.

For Czochralski pulling we used the equipment as described recently.[12] Crystals were pulled from a 22 (Ø) × 25 mm Ir crucible under a constant Ar flow of 50 ml/min. $CaCO_3$ (Aldrich, purity: 99.95%), $CaHPO_4$ (Aldrich, purity: 99%), and $CaF_2$ (Aldrich, purity: 99.9%) were used as starting materials. In a first step stoichiometric amounts of the raw materials were shaken in a polyethylene bottle and sintered in a platinum crucible at 1100 °C for 60 h in a $N_2$ flow of about 100 ml/min. Crystals grown from a charge prepared in this way were opaque and consisted of at least two phases. A possible explanation is given by the Reaction (1):

$$3CaHPO_4(s) + CaCO_3(s) + CaF_2(s) \rightarrow Ca_5(PO_4)_3F(s) + H_2O(g) + CO_2(g) + HF(g). \quad (1)$$

Formation of $H_2O$ yielded a certain amount of hydroxyapatite in the starting powder, which led to inclusions during crystal growth. Precursor material was hence prepared in two steps: (i) water-free $Ca_3(PO_4)_2$ was obtained first according to Reaction (2) in air at a

 

temperature of 1000 °C (60–80 h).

$$2CaHPO_4(s) + CaCO_3(s) \rightarrow Ca_3(PO_4)_2(s) + H_2O(g) + CO_2(g). \quad (2)$$

In a second step (ii), $Ca_3(PO_4)_2$ obtained from Reaction (2) and $CaF_2$ were reacted. The latter was dried under a flow of 5% HF/95% $N_2$ gas (20–50 ml/min) at 1000 °C for 24 h. To prevent water contamination, the $Ca_3(PO_4)_2$ powder was taken from the furnace directly after finishing Reaction (2). Hot $Ca_3(PO_4)_2$ was mixed with the $CaF_2$ in a preheated mortar. After transferring into a hot Ir crucible, it was heated up in 2 h to 1700 °C in order to complete Reaction (3):

$$3Ca_3(PO_4)_2(s) + CaF_2(s) \rightarrow 2Ca_5(PO_4)_3F(s). \quad (3)$$

For Reactions (2) and (3) stoichiometric amounts of the starting materials were used. The melt (11–13 g) was superheated for 1 h 50 °C above the melting point. Spontaneous nucleation was initiated on a tapered Ir wire and crystals became single grain after ~2 mm of pulling. Spontaneous nucleation and seed selection produced crystals growing along the *c*-axis. For a pulling rate of 1.2 mm/h and a rotation of 45 rpm pale blue-greenish crystals of 30 mm in length and 10 mm in diameter were obtained. The boules showed opaque inclusions in the core extending along the *c*-axis. These defects may be caused by a lower curvature of the convex growth interface at larger diameters. The trapping of gas bubbles in the core of Ca-FAP crystals is a known imperfection.[4] Slices with sufficient optical quality for spectroscopic measurements could be cut from the obtained crystals.

During growth experiments (24 h) vapor losses, which may lead to the described imperfections in the core of the crystal, were observed. Electron microprobe (EMP) and powder diffraction analysis of the losses, which were collected from the wall of the Czochralski apparatus, showed that substantial amounts of $CaF_2$ are lost during growth. In order to minimize these losses, an insulation lid (mullite) was placed at about 50 mm above the top of the crucible. Additionally, this particular insulation reduced the axial temperature gradient down to ~20–30 °C/cm. This was important to avoid cracking during the cooling process. A further precaution which proved to be a determinant in avoiding cracks was a slow cooling rate of 25 °C/h.

For doping experiments $Pr_6O_{11}$ (Fluka, purity: 99.9%) or $Yb_2O_3$ (Fluka, purity: 99.9%) was added to the melt. Other growth parameters were the same as for pure Ca-FAP.

Small pieces of a crystal grown at a $Pr^{3+}$ concentration in the melt of $c_0 = 0.07$ mol % (according to all atoms of Ca-FAP) were dissolved in $HNO_3$ (0.7 molar) and analyzed with the inductively coupled plasma optical emission spectroscopy (ICP). The ICP technique led to $c_{Pr} = 0.1$ mol % in the crystal. Solutions of $PrCl_3 \cdot 6H_2O$ (Janssen Chemica, purity: 99.9%) in $HNO_3$ (0.7 molar) were used for calibration. An EMP analysis of a boule grown at $c_0 = 0.07$ mol % $Pr^{3+}$ yielded a doping level of $c_{Pr} = 0.14$ mol %. In the case of the EMP measurement $PrAlO_3$ served as a reference for $Pr^{3+}$. The difference in the $Pr^{3+}$ concentrations may originate from the reference material used in the EMP analysis. $PrAlO_3$ contains different elements when compared to Ca-FAP : $Pr^{3+}$ and therefore, the software of the EMP calculated a different correction factor for the reabsorption of the characteristic x-ray of the $Pr^{3+}$. We assume that $k_{eff} = c_{Pr}/c_0 = 1.4$ obtained by the ICP method is more accurate.

The concentration for $Yb^{3+}$ doping was determined spectroscopically. Based on the cross sections $\sigma$ for the lines at 905 and 982 nm originating from the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of $Yb^{3+}$ and the measured absorbance at the maximums of these lines, the doping level was calculated. A sample grown at $c_0 = 0.28$ mol % $Yb^{3+}$ and 0.5 mol % $Na^+$ in the melt was cut with flat and parallel faces perpendicular to the *c*-axis for absorption measurements with unpolarized light at room temperature (Fig. 1). With $\sigma_{905nm} = 2.6 \cdot 10^{-20}$ cm$^2$ and $\sigma_{982nm} = 5.3 \cdot 10^{-20}$ cm$^2$ for an electric field polarization perpendicular to the *c*-axis ($E \perp c$),[13] we yielded $c_{Yb} = 0.13$ mol %, which corresponds to $k_{eff} = 0.5$.

Qualitatively, the influence of cations co-doping has been observed earlier.[14] The value of $k_{eff}$ for $Yb^{3+}$ seems not to be significantly influenced by adding $Na^+$ to the melt. This is also consistent with the fact that we could not detect $Na^+$ by the proton induced gamma emission (PIGME)[15] method in a crystal grown at melt concentrations $c_0 = 0.6$ mol % $Na^+$ and 0.3 mol % $Yb^{3+}$. The detection limit was 0.03 mol % $Na^+$ and a basalt (BHVO-1)[16] served as Na reference.

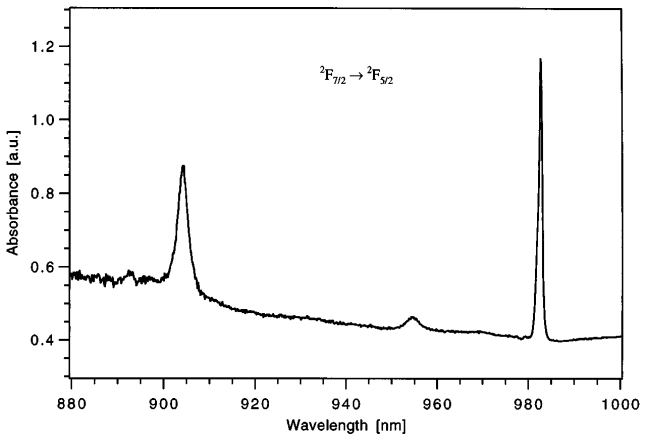


FIG. 1. Optical absorption spectrum of $Yb^{3+}$ doped Ca-FAP ($c_{Yb} = 0.13$ mol %) at room temperature. The thickness of the sample was 3.24 mm and the spectrum was measured with unpolarized light propagating along the *c*-axis.

A possible explanation for a large difference in the $k_{\text{eff}}$ for $Yb^{3+}$ and $Pr^{3+}$ could be due to the different ionic radii of the lanthanides. The electronic structures are very similar and the oxidation states are the same. The only variable affecting $k_{\text{eff}}$ is most likely the ionic radii (0.98 Å for $Yb^{3+}$ and 1.14 Å for $Pr^{3+}$, for a coordination number of 8).[17] Brice[18] regards the lattice as an elastic continuum and calculates the strain energy originating from the radius misfit between the substituted and the doping ion. The effective distribution coefficient $k_{\text{eff}}$ depends on the misfit in the radius and on elastic properties:

$$\ln(k_{\text{eff}}) = \ln(k_0) - \frac{4\pi E N_{\text{A}}}{RT} \times \left[\frac{1}{2} r_A (r_j - r_A)^2 + \frac{1}{3}(r_j - r_A)^3\right], \quad (4)$$

where $k_0$ is the effective distribution coefficient for a dopant with a radius misfit of zero, $E$ is the averaged Young's modulus, $N_{\text{A}}$ is the Avogadro number, $T$ is the melting temperature of the material and $r_A$ and $r_j$ are the effective ionic radii of the substituted ion (index $A$) and the dopant (index $j$), respectively. Relation (4) was applied to estimate the ratio between the distribution coefficients of $Yb^{3+}$ and $Pr^{3+}$ ($k_{\text{eff}}^{\text{Yb}}/k_{\text{eff}}^{\text{Pr}} = 0.58$) using an effective ionic radius of 1.12 Å (for a coordination number of 8)[17] for $Ca^{2+}$. Young's moduli for the direction parallel $(E_{\parallel})$ and perpendicular $(E_{\perp})$ to the 6-fold symmetry axis were calculated from the elastic constants of hydroxy-apatite.[19] The average value $E = \frac{1}{3} \cdot (E_{\parallel} + 2 \cdot E_{\perp}) = 120$ GPa was used for Eq. (4). Payne *et al.*[13] give an average value of $E = 119$ GPa for $Ca_5(PO_4)_3F$. The measured ratio of the two distribution coefficients is 0.36, being smaller than the calculated value (0.58). This may be caused by an uncertainty in the ionic radii, which after Brice[18] can introduce an error of 20%. However, the model predicts a significantly larger $k_{\text{eff}}$ for $Pr^{3+}$.

Optical absorption spectra for a $Pr^{3+}$ doped crystal ($c_{\text{Pr}} = 0.1$ mol %) at room temperature to 11 K measured with unpolarized light propagating along the $c$-axis indicated that the linewidth of the $^3H_4 \rightarrow {}^1D_2$ transition exhibits only a low temperature dependence (Fig. 2). The half-width is decreasing only by a factor 1.4 (for the lowest crystal field level), which would mean that the broadening is mainly inhomogeneous. The room temperature absorption spectrum of an $Yb^{3+}$ doped sample ($c_{\text{Yb}} = 0.13$ mol %) exhibits a half-width of 2.49 nm for the line at 905 nm ($E \perp c$) (Fig. 1). This is in agreement with the values of 2.4 nm (for $E \| c$) obtained earlier.[20,21]

Preliminary experiments[22] on Ca-FAP : $Pr^{3+}$ revealed no H-OHB processes. Maybe this is due to (i) the site symmetry $m$ of the $Pr^{3+}$ ion, which does not allow the transition in the lowest crystal field level,[10] or (ii) the presence of a broad homogeneous line leading to an overlapping of the holes with the other hyperfine levels of the electronic ground state.

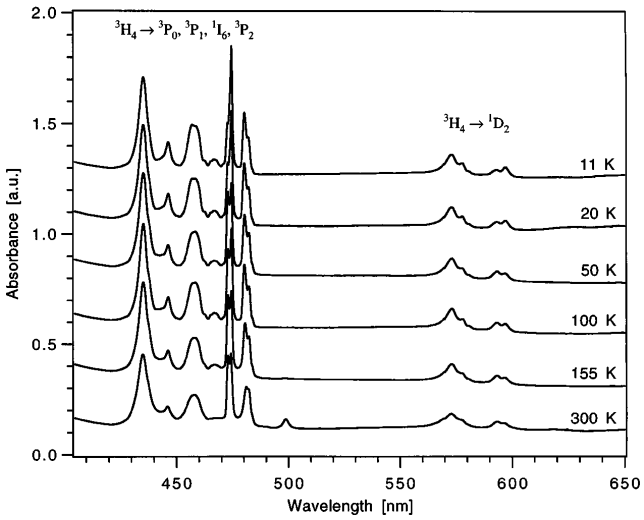


FIG. 2. Optical absorption spectra of $Pr^{3+}$ doped Ca-FAP ($c_{\text{Pr}} = 0.1$ mol %) at 11 to 300 K. The thickness of the sample was 3.1 mm. All spectra were measured with unpolarized light propagating along the $c$-axis.

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